

[54] USE OF LIQUID-CRYSTAL
5-PHENYLPYRIMIDINE DERIVATIVES AS
COMPONENTS OF SMECTIC
LIQUID-CRYSTAL MIXTURES

[75] Inventors: Hans-Rolf Dübal,
Königstein/Taunus; Claus Escher,
Mühlthal; Wolfgang Hemmerling,
Sulzbach (Taunus); Ingrid Müller,
Hofheim am Taunus; Dieter
Ohlendorf, Liederbach; Rainer
Wingen, Hattersheim am Main, all of
Fed. Rep. of Germany

[73] Assignee: Hoechst Aktiengesellschaft,
Frankfurt am Main, Fed. Rep. of
Germany

[21] Appl. No.: 378,470

[22] Filed: Jul. 12, 1989

Related U.S. Application Data

[63] Continuation of Ser. No. 171,565, Mar. 22, 1988, abandoned.

[30] Foreign Application Priority Data

Mar. 24, 1987 [DE] Fed. Rep. of Germany 3709549

[51] Int. Cl.⁴ G02F 1/13; C09K 19/34

[52] U.S. Cl. 252/299.61; 252/299.01;
350/350 R; 350/350 S

[58] Field of Search 252/299.61, 299.01;
350/350 R, 350 S; 544/318, 315, 242, 335

[56] References Cited

U.S. PATENT DOCUMENTS

4,565,425	1/1986	Petrzilka	252/299.61
4,676,604	6/1987	Petrzilka et al.	252/299.61
4,776,973	10/1988	Bofinger et al.	252/299.61
4,780,241	10/1988	Furukawa et al.	252/299.61
4,818,428	4/1984	Schenble et al.	252/299.61
4,820,839	4/1989	Krause et al.	252/299.61
4,834,904	5/1984	Krause et al.	252/299.61

FOREIGN PATENT DOCUMENTS

199004 10/1986 European Pat. Off. 252/299.61

206228 12/1986 European Pat. Off. 252/299.61
225195 6/1987 European Pat. Off. 252/299.61
260077 3/1988 European Pat. Off. 252/299.61

(List continued on next page.)

OTHER PUBLICATIONS

Zaschke, H., Advances in Liquid Crystal Research & Applications, Bata, L., Ed., Pergamon Press, Oxford, pp. 1059-1074 (1980).

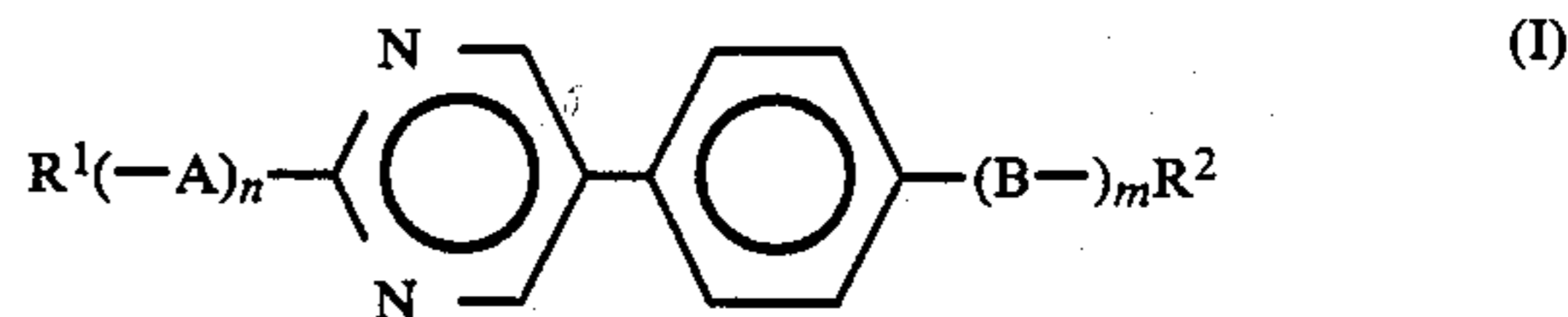
Demus, D. et al., Flüssige Kristalle in Tabellen II, veb Deutscher Verlag für Grundstoffindustrie, Leipzig, pp. 376-379 (1984).

(List continued on next page.)

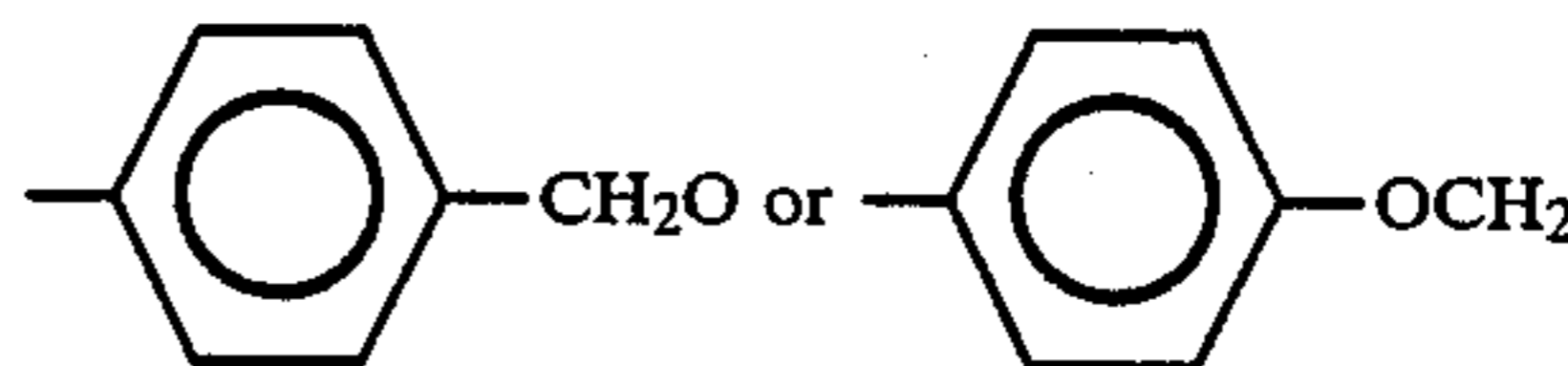
Primary Examiner—Teddy S. Gron
Attorney, Agent, or Firm—Curtis, Morris & Safford

[57] ABSTRACT

The compounds of the general formula (I)



are particularly highly suitable as components of smectic, liquid-crystal mixtures, the symbols having the following meaning: R¹ and R² denote identical or different, straight-chain or branched alkyl or alkenyl groups which can contain asymmetric carbon atoms, containing 2 to 16 carbon atoms, in which one or more non-adjacent —CH₂— groups can be replaced by —O— and/or —S—, —A and —B each denote group



in which the radicals R¹, R², in each case, are situated at the phenylene part of —A, —B and m and n denote 0 or 1, but m+n is always zero or 1.

5 Claims, 1 Drawing Sheet

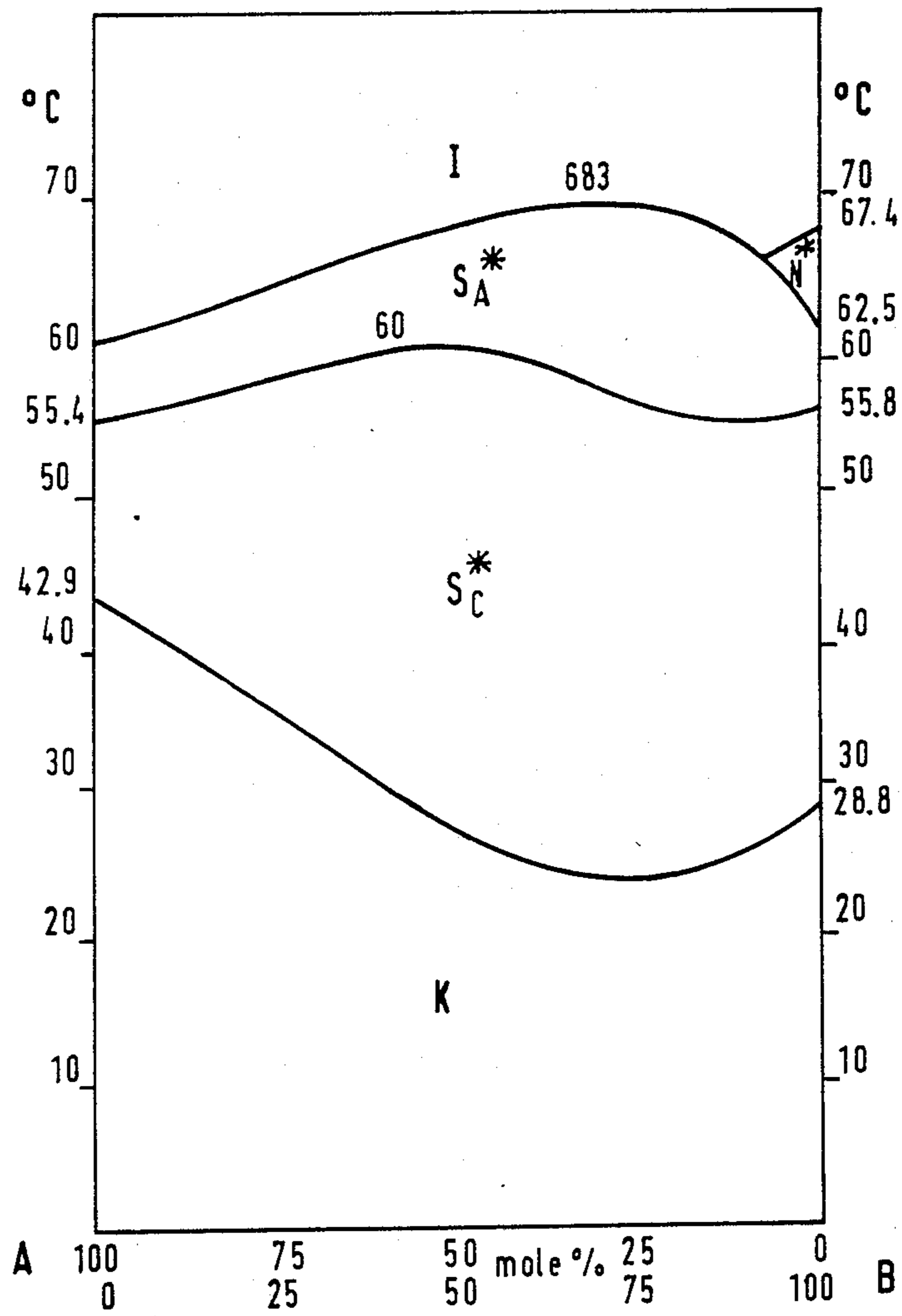
FOREIGN PATENT DOCUMENTS

269062 6/1988 European Pat. Off. 252/299.61
3500897 7/1982 Fed. Rep. of
Germany 252/299.61
3506446 8/1986 Fed. Rep. of
Germany 252/299.61
3515373 11/1986 Fed. Rep. of
Germany 252/299.61
3515374 11/1986 Fed. Rep. of
Germany 252/299.61
3518734 11/1986 Fed. Rep. of
Germany 252/299.61

63-48270 2/1988 Japan 252/299.61
86/06401 11/1986 World Int. Prop. O. 252/299.61
87/05018 8/1987 World Int. Prop. O. 252/299.61

OTHER PUBLICATIONS

Sharma, N. K. et al., Molecular Crystals Liq. Cryst.,
vol. 151, pp. 225-231 (1987).
Zaschke et al., Chemical Abstracts, vol. 87, p. 608,
184456d (1977).
Mueller et al., Chemical Abstracts, vol. 110, p. 659,
67361b (1989).



**USE OF LIQUID-CRYSTAL
5-PHENYLPYRIMIDINE DERIVATIVES AS
COMPONENTS OF SMECTIC LIQUID-CRYSTAL
MIXTURES**

This application is a continuation of application Ser. No. 171,565, filed Mar. 22, 1988 now abandoned.

Liquid crystals have, particularly in the last decade, been introduced into a wide range of technical fields in which electrooptical and display device properties are in demand (for example in watch, pocket-calculator and typewriter displays). These display devices are based on the effects of dielectric alignment in the nematic, cholesteric and/or smectic phases of liquid-crystal compounds, the molecular longitudinal axis of the compounds, due to the dielectric anisotropy, adopting a preferred alignment in an applied electrical field. The usual switching times in these display devices are rather too slow for many other potential areas of application of liquid crystals, which are per se highly promising chemical compounds for industry due to their unique properties. This disadvantage is particularly noticeable if it is necessary to address a large number of image points, which means that the production costs of instruments containing relatively large areas, such as video equipment, oscillographs or TV, radar, EDP or word processor screens, would be too high.

Besides the nematic and cholesteric liquid crystals, ferroelectric, smectic liquid-crystal phases have in the last few years become increasingly important.

Clark and Lagerwall have been able to show that the use of such liquid-crystal systems in very thin cells leads to optoelectric switching or display elements which, compared to conventional TN ("twisted nematic") cells have switching times which are faster by a factor of about 1,000 (cf. for example Lagerwall et al. "Ferroelectric Liquid Crystals for Displays", SID Symposium, October Meeting 1985, San Diego, Calif., USA). As a consequence of these and other favorable properties, for example the possibility of bistable switching and the contrast which is virtually independent of the view angle, FLCs are generally highly suitable for the above mentioned areas of application, for example via matrix addressing.

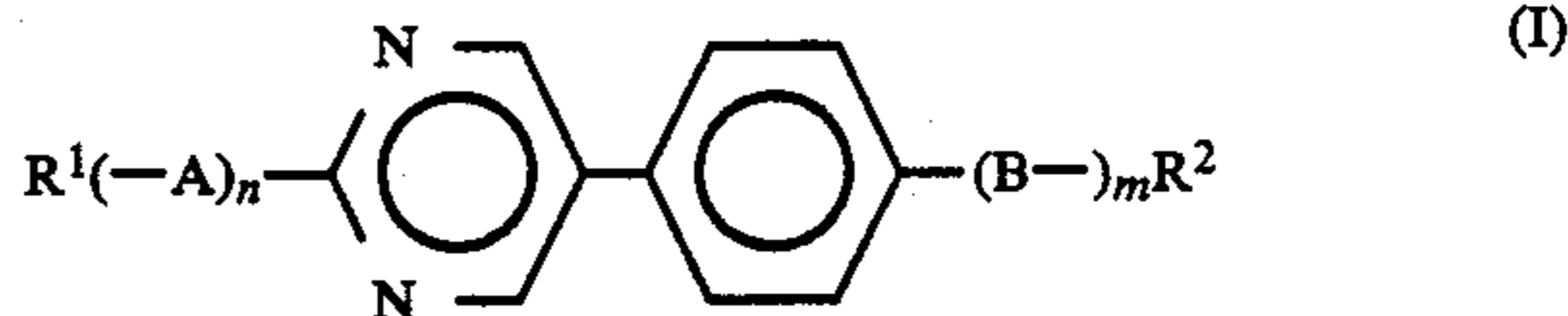
For practical use of ferroelectric liquid crystals in optoelectric displays, chiral, tilted smectic phases, for example S_c^* phases, are required (R. B. Meyer, L. Liébert, L. Strzelecki and P. Keller, *J. Physique* 36, L-69 (1975)), which are stable over a large temperature range.

This goal can be achieved using compounds which themselves form chiral smectic phases, for example S_c^* phases or, on the other hand, by doping non-chiral compounds which form tilted smectic phases with optically active compounds (M. Brunet, Cl. Williams, *Ann. Phys.* 3, 237 (1978)).

Therefore, there is a demand for compounds which form smectic phases and by means of which mixtures forming smectic, in particular S_c or S_c^* phases, can be prepared.

A great disadvantage of most currently available substances forming tilted smectic phases, in addition to the phase range limited in terms of temperature, is a low chemical, thermal or photochemical stability and a large positive dielectric anisotropy which is unfavorable for most applications.

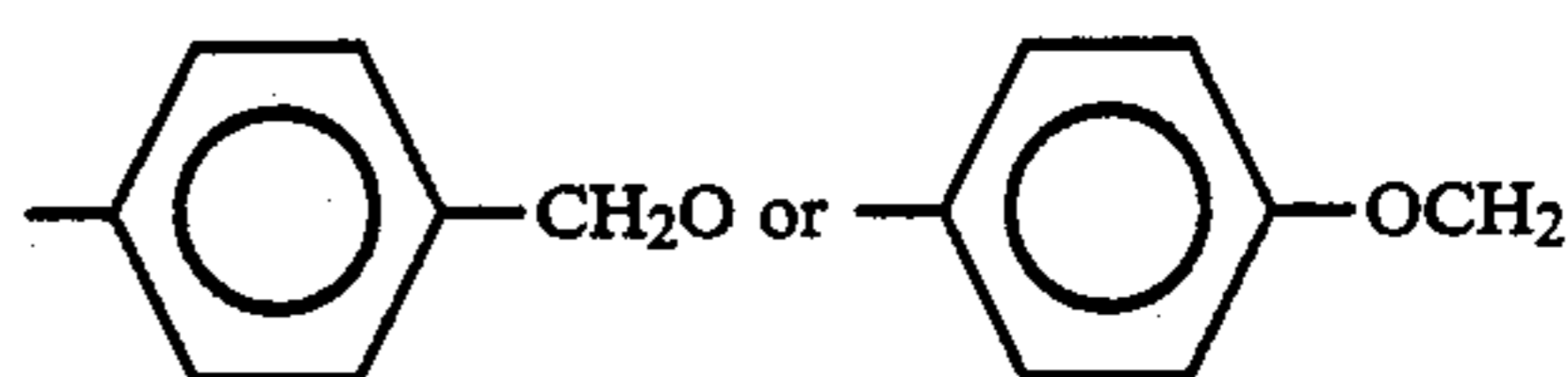
It has now been found that compounds which are particularly well suited as components of smectic, liquid-crystalline mixtures are those of the general formula (I)



the symbols having the following meanings:

R^1 and R^2 denote identical or different, straight-chain or branched alkyl or alkenyl groups which can contain asymmetric carbon atoms, containing 2 to 16 carbon atoms, in which one or more non-adjacent $-\text{CH}_2-$ groups can be replaced by $-\text{O}-$ and/or $-\text{S}-$,

$-A$ and $-B$ each denote



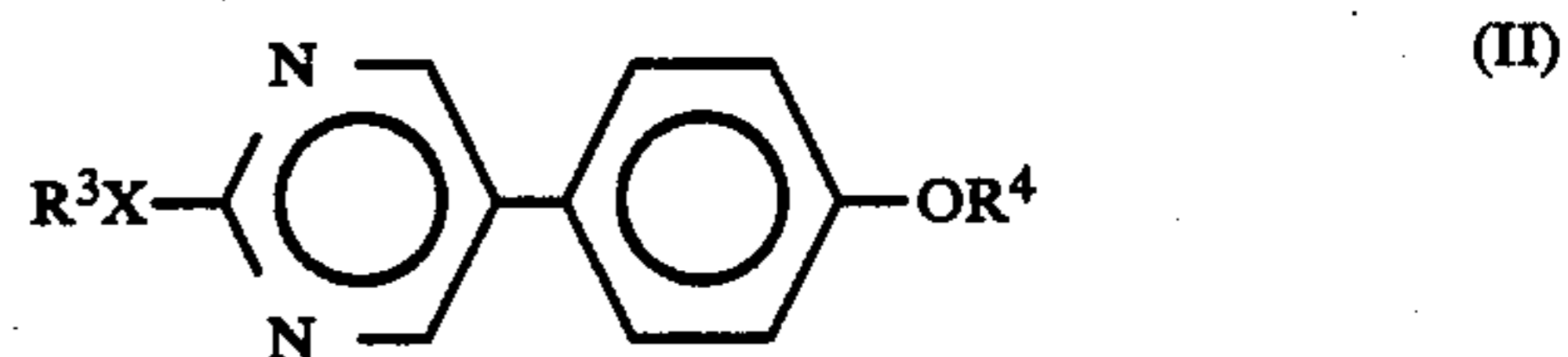
in which the radicals R^1 , R^2 , in each case, are situated at the phenylene part of $-A$, $-B$ and

m and n denote 0 or 1, but $m+n$ is always zero or 1.

These compounds have a high chemical, thermal and photochemical stability. In addition, they have a negative or only a slight positive dielectric anisotropy (cf. Examples 1 to 3). Therefore, the dielectric properties of mixtures are favorably affected by components of the formula (I).

Moreover, chiral compounds of formula (I) also have a positive effect on the ferroelectric properties of the mixtures containing them, since they themselves already have good ferroelectric properties (Examples 1 and 8).

Particular preference is given to compounds of formula (I) having the special form (II)



in which X has the meaning of $-\text{O}$, $-\text{S}$ or denotes a single bond and R^3 , R^4 each denotes identical or different, straight-chain or branched alkyl or alkenyl groups (including groups with or without asymmetric carbon atoms) having 7 to 14 carbon atoms.

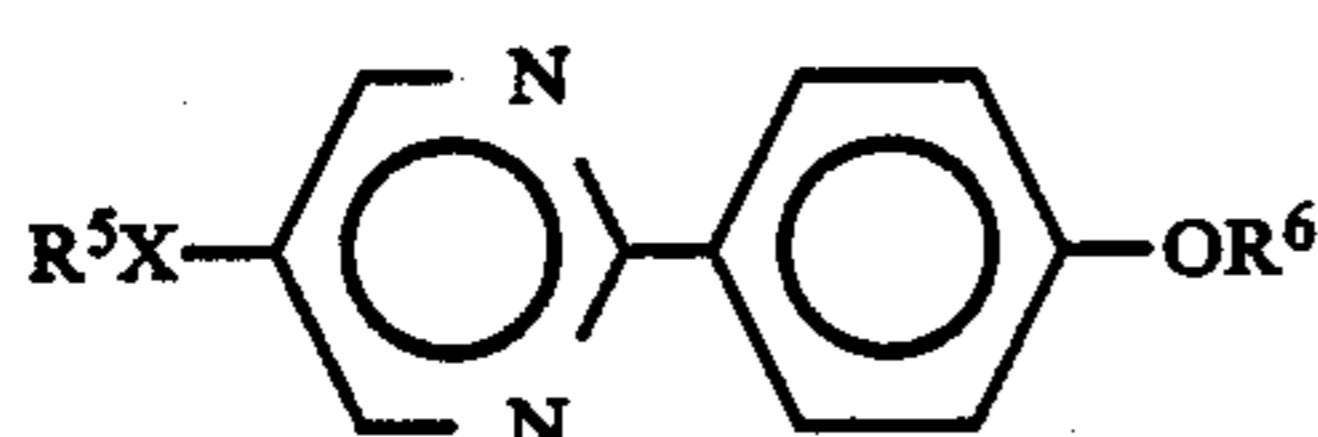
Incidentally, it has been found that compounds of formula (II) form liquid-crystal S_c or S_c^* phases. To a large extent, they even have, in terms of temperature, very broad and predominantly favorable S_c or S_c^* ranges, that is ranges which are located at relatively low temperatures. This finding is the more surprising, since, based on common knowledge (for example "Flüssige Kristalle in Tabellen" (Liquid crystals in tables), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, Volume I (1974), Volume II (1984)), the appearance of S_c or S_c^* phases was not to be expected in compounds of formula (I) or (II).

Moreover, the compounds of formula (II) also have in many cases a S_A phase in addition to the S_c or S_c^* phase which is very advantageous for their use. Com-

pounds of formula (II) are therefore preferred components of chiral, smectic C phases (S_c^*).

Preference is further given to compounds of formula (I) having $n=1$ or $m=1$. Most of these compounds have S_c or S_c^* phases and are suitable as mixing components in particular for expanding the S_c or S_c^* range to higher temperatures in combination with an advantageous effect on the dielectric behavior of the mixture.

It is particularly preferred to use compounds of formula (II) in S_c or S_c^* mixtures together with compounds of the known type



in which $X=O$ or denotes a single bond and R^5 , R^6 are identical or different alkyl groups having 6 to 15 carbon atoms.

This is because it has been found, quite surprisingly, that the combined use of compounds of formula (II) and formula (III) can lead to an expansion of the S_c or S_c^* phase not only to lower but also to higher temperatures (induced S_c , cf. Example 3). This behavior is extremely unusual and advantageous for use.

The preparation of the compounds to be used according to this invention has been described in DE-A 3,709,618.

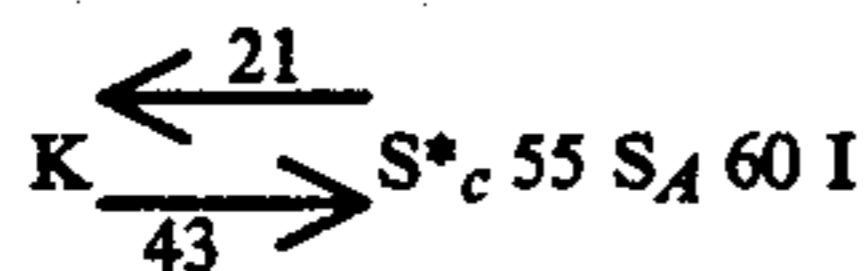
BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 represents the binary phase diagram of compound A, (S)-2-octylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine, admixed with compound B, 5-octyl-2-(4-octyloxyphenyl)pyrimidine, plotting temperature versus mole %.

The following examples are intended to illustrate the invention.

EXAMPLE 1

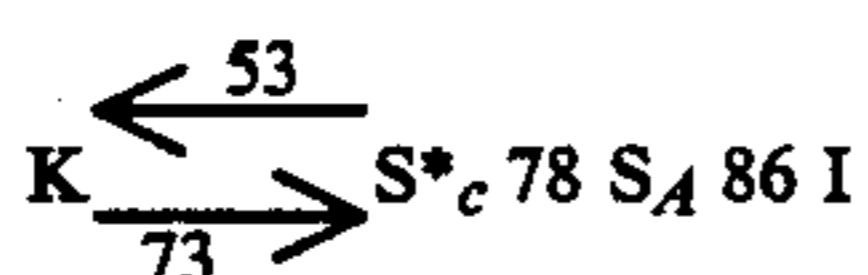
(S)-2-Octylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine has the phase sequence



and at 40° C. a spontaneous polarization of 1.5 nC/cm² and has a switching time of 200 μ s at an applied square voltage of 10 V_{eff}/μ m. The tilting angle at this temperature is 25° and the dielectric anisotropy at 10 kHz is $\Delta\epsilon = -0.6$.

EXAMPLE 2

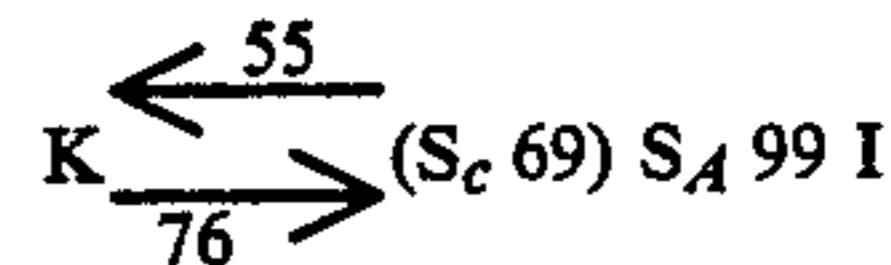
(S)-2-Octyloxy-5-[4-(6-methyloctyloxy)phenyl]pyrimidine has the phase sequence



and the dielectricity constants ϵ'' (homeotropic orientation) and ϵ_{\perp} (planar orientation) at 10 kHz and 75° C.: $\epsilon'' = 3.5$, $\epsilon_{\perp} = 3.8 \rightarrow \Delta\epsilon = -0.3$.

EXAMPLE 3

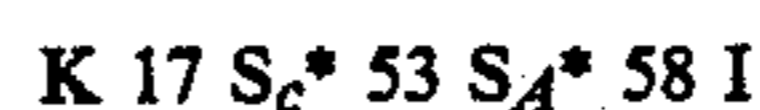
2-Octyloxy-5-(4-octyloxyphenyl)pyrimidine has the phase sequence



and the dielectricity constants parallel and perpendicular to the director (10 kHz, 75° C.) $\epsilon'' = 3.79$, $\epsilon_{\perp} = 3.9 \rightarrow \Delta\epsilon = -0.11$.

EXAMPLE 4

A mixture consisting of 50% of (S)-2-decylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine 50% of (S)-2-octylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine has the following phase sequence:



EXAMPLE 5

A mixture consisting of 30% of 5-decyl-2-(4-decyloxyphenyl)pyrimidine 55% of 5-octyl-2-(4-octyloxyphenyl)pyrimidine 10% of 5-decyl-2-(4-octyloxyphenyl)pyrimidine 5% of 2-octyloxy-5-[4-(4-decyloxyphenyl)methoxyphenyl]pyrimidine can be undercooled up to +7° C. and has the phase sequence $S_c 53 S_A$ and $S_A 71 I$

EXAMPLE 6

A mixture consisting of (S)-2-octylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine (A) and the compound 5-octyl-2-(4-octyloxyphenyl)pyrimidine (B) which is known from the literature (Flussige Kristalle in Tabellen (Liquid crystals in tables), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974) and is not covered by formula (I), shows the following characteristic:

The highly surprising and extremely advantageous behavior upon mixing the two above mentioned substances can be seen from the binary phase diagram (heating curves) in the figure: the S_c^* phase is expanded not only to low but also to high temperatures. This latter behavior has heretofore not been described before.

EXAMPLE 7

A mixture consisting of 80% of (S)-2-heptylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine 20% of (S)-2-nonyloxy-5-[4-(6-methyloctyloxy)phenyl]pyrimidine can be undercooled to less than -20° C. and has the phase sequence.



EXAMPLE 8

A mixture consisting of 45% of (S)-2-decylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine 45% of (S)-2-octylthio-5-[4-(6-methyloctyloxy)phenyl]pyrimidine 10% of (R)-2-methylpropyl N-4-(4-octyloxybenzoyloxy)benzoyl-(S)-prolinate

5

has a S_c^* phase in the range from 10° C. to 42° C. and a spontaneous polarization of +30 nC/cm² at 25° C. and has a switching time in the SSFLC display of 45 μs at an applied square voltage of 10 V_{eff}/μm.

EXAMPLE 9

A mixture consisting of
 40% of (S)-2-decylthio-5-[4-(6-methyloctyloxy)-phenyl]pyrimidine
 40% of (S)-2-octylthio-5-[4-(6-methyloctyloxy)phenyl]-pyrimidine
 2% of 5-undecyl-2-(4-decyloxyphenyl)pyrimidine
 2% of 5-decyl-2-(4-octyloxyphenyl)pyrimidine
 5.5% of 5-decyl-2-(4-decyloxyphenyl)pyrimidine
 10.5% of 5-octyl-2-(4-octyloxyphenyl)pyrimidine
 has a melting point of 5° C. and has a phase sequence of

$S_I^* 18 S_c^* 58 S_A 62 I$

EXAMPLE 10

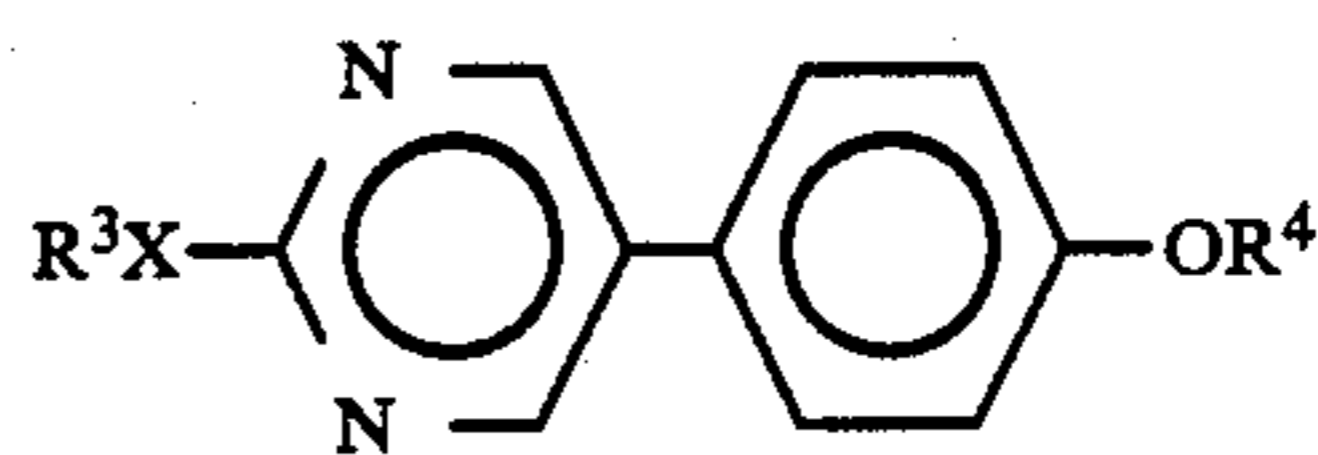
A mixture consisting of
 1.3% of (S)-2-(4-decyloxybenzyloxy)-5-[4-(6-methyloxy)phenyl]pyrimidine
 39.5% of 4-(4-methylhexyloxy)phenyl (R,S)-4-decyloxybenzoate
 32.6% of 5-octyl-2-(4-octyloxyphenyl)pyrimidine
 16% of 5-decyl-2-(4-decyloxyphenyl)pyrimidine
 10.6% of 5-decyl-2-(4-octyloxyphenyl)pyrimidine
 has the phase sequence

$K 3 S_c^* 62 S_A 68 N^* 69 I$

We claim:

6

1. Smectic, liquid-crystal mixtures, comprising compounds of the formula (I)



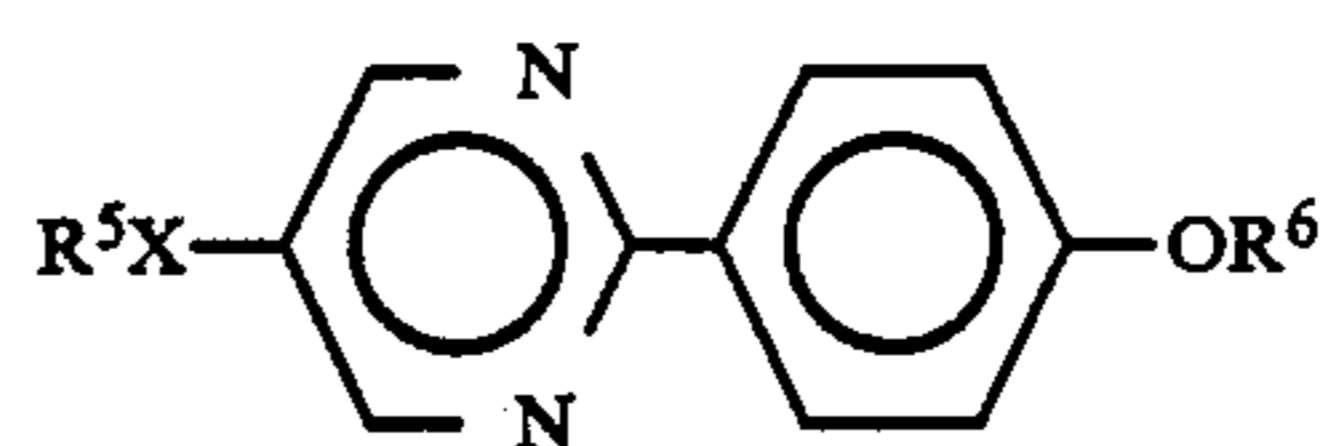
10 in which X is a single bond, —O or —S, and R³ and R⁴ are identical or different, straight-chain or branched alkyl groups having 7 to 14 carbon atoms which can contain asymmetric carbon atoms.

2. Mixtures as claimed in claim 1, having chiral, smectic liquid-crystal phases.

3. Mixtures as claimed in claim 1, having chiral, tilted smectic liquid-crystal phases.

4. Mixtures as claimed in claim 1, having chiral, smectic C phases (S_c^*).

5. Smectic, liquid-crystal mixtures having S_c or S_c^* phases comprising a combination of compounds of formula (I) as claimed in claim 1 with compounds of the formula (II),



30 in which X is a single bond or —O, and R⁵ and R⁶ are identical or different alkyl groups having 6 to 15 carbon atoms.

* * * * *

35

40

45

50

55

60

65